[1] The publication of this paper, written in 1924, was delayed because the authors were busy with other work. The recent discovery made by Davisson and Germer (*Nature*, **119**, p. 558, 1927) gives to the problem of corpuscular diffraction a new interest and importance.

[2] P. S. Epstein and P. Ehrenfest, these PROCEEDINGS, **10**, p. 133, 1924.

[3] Cf., for instance, *Enzyklopädie der Math.*, Wiss.

[4] M. Planck, "Theorie der Wärmestrahlung," Formula (64). The factor 2 in Planck's formula arises from his considering a perfectly reflecting element, while we have a perfectly absorbing one.

[5] Since this was written, the work of de Broglie and Schroedinger has brought us much nearer to the solution of these problems.

ABSOLUTE INTENSITIES IN THE HYDROGEN-CHLORIDE ROTATION SPECTRUM

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The development of new quantum theories which purport to furnish a means for the prediction of the absolute intensities of spectral lines makes it important to determine these intensities experimentally in such cases as may be theoretically treated. One of these few is the pure rotation spectrum as, for example, that of hydrogen chloride recently determined in absorption by Czerny.[1] This spectrum was used by Tolman and Badger[2] in the calculation of integral absorption coefficients, and so for the determination of the experimental B_{ij}'s or the probabilities of transition from one energy state of rotation to the next higher in the presence of radiation which may be absorbed. Since, however, this spectrum was investigated with a spectrometer of not very great resolving power, this process may have led to somewhat inaccurate results. In the present article are described new experimental measurements on the same spectrum, and an improved method whereby they are used to determine absolute absorption coefficients.

If the absorption is measured at several pressures, keeping the path length constant, an indirect method can be used for evaluating $\int \alpha(\nu)d\nu$, which avoids the difficulties due to low resolving power. Suppose that the intensity of the background radiation used in the absorption experiments is the function of wave-length $I_0(\lambda)$. If now the center of the spectrometer slit is set on the wave-length λ_s, radiation of other wave lengths between the limits of say $\lambda_s + S$ and $\lambda_s - S$ will be falling on the thermocouple due to the finite slit width. We may make the reasonable assumption that the intensity of such light of wave-length $\lambda_s + \delta$ will

be given by the product of $I_0(\lambda_s + \delta)$ and of $f(\delta)$ a function characteristic of the spectrometer. Thus at this setting the total light falling on the thermocouple is given by

$$D = \int_{-S}^{+S} I_0(\lambda_s + \delta) f(\delta) d\delta \qquad (1)$$

and the observed galvanometer reading at this setting will be a measure of this quantity. At the same setting of the spectrometer, but with HCl in the absorption cell, the deflection will be a measure of $\int_{-S}^{+S} I(\lambda_s + \delta)$-$(\delta)d\delta$ where $I(\lambda)$ represents the intensity distribution in the new spectrum.

Now the difference in galvanometer deflections at a given setting, with the absorption cell evacuated and again when filled with gas, will be given by the following equation.

$$A = \int_{-S}^{+S} [I_0(\lambda_s + \delta) - I(\lambda_s + \delta)] f(\delta) d\delta. \qquad (2)$$

This quantity may be measured at several spectrometer settings, plotted as a function of λ_s, and a graphical integration will give, if we expand in δ and then group terms in powers of δ,

$$\int_{\lambda_1}^{\lambda_2} A d\lambda_s = \int_{\lambda_1}^{\lambda_2} \int_{-S}^{+S} \left\{ [I_0(\lambda_s) - I(\lambda_s)] + \left[\frac{dI_0(\lambda)}{d\lambda} - \frac{dI(\lambda)}{d\lambda} \right]_{\lambda=\lambda_s} \cdot \delta + \ldots \right\} f(\delta) d\delta d\lambda_s. \qquad (3)$$

If the absorption spectrum contains only one line which is narrow, on either side of this line the function I approaches I_0, and the two become practically identical at λ_2 and λ_1 if these limits are chosen sufficiently greater and smaller, respectively, than λ_0 the center of the line. At these limits the derivatives of the two functions will also become equal. Consequently all of the right-hand member of equation (3) vanishes, except as given in the following equation

$$\int_{\lambda_1}^{\lambda_2} A d\lambda_s \doteq \int_0^{\infty} [I_0(\lambda) - I(\lambda)] d\lambda \int_{-S}^{+S} f(\delta) d\delta. \qquad (4)$$

Now since we are interested in the probability of absorption by an isolated molecule, let us define β as the fraction of energy absorbed per molecule encountered in the path of a parallel beam of radiation of unit cross section. Evidently the diminution in intensity as the light traverses a differential path is given by

$$-dI(\lambda) = I(\lambda)\beta(\lambda,p)dN \qquad (5)$$

since β will depend on the proximity of molecules to one another. It follows that

$$I_0(\lambda) - I(\lambda) = I_0(\lambda)(1 - e^{-\beta(\lambda,p)N}) \tag{6}$$

when the beam has traversed a path containing N molecules. Combination with equation (4) yields the following relation

$$\frac{1}{\int f(\delta)d\delta}\int_{\lambda_1}^{\lambda_2} Ad\lambda \doteq \int_0^{\infty} I_0(\lambda)(1 - e^{-\beta(\lambda,p)N})d\lambda. \tag{7}$$

If we introduce the perfect gas law, differentiation with respect to pressure yields, if x is the length of the absorption vessel

$$\frac{1}{\int f(\delta)d\delta}\frac{d}{dp}\int_{\lambda_1}^{\lambda_2} Ad\lambda \doteq \int^{\infty} I_0(\lambda)e^{-\beta(\lambda,p)\frac{px}{kT}}\left\{\frac{\partial\beta}{\partial p}\cdot\frac{px}{kT} + \beta(\lambda,p)\frac{x}{kT}\right\}d\lambda. \tag{8}$$

And at zero pressure, if we may assume I_0 constant across the relatively narrow absorption line

$$\frac{kT}{xI_0(\lambda_0)\int f(\delta)d\delta}\frac{d}{dp}\int_{\lambda_1}^{\lambda_2} Ad\lambda \doteq \int_0^{\infty}\beta(\lambda, o)d\lambda. \tag{9}$$

The left-hand member of the equation is experimentally determinable. $\int Ad\lambda$ is defined above. The quantity $I_0\ (\lambda_0)\int f(\delta)d\delta$ is measured by the galvanometer deflection when the spectrometer is set on λ_0 provided I_0 may be regarded as linear across the slit width, as may be seen from equation (1).

Now the ordinary absorption coefficient α, defined for atmospheric pressure with the path expressed in centimeters, is evidently related to β by the expression given below, provided the *integral* absorption coefficient would be unchanged in value if the effect of intermolecular forces could be decreased to zero.

$$\int \alpha(\lambda)d\lambda = n\int \beta(\lambda, o)d\lambda = \frac{p}{kT}\int \beta(\lambda, o)d\lambda \tag{10}$$

where n is the number of molecules per cubic centimeter under the conditions of the measurement of α.

We have made a determination of the absorption of hydrogen chloride in the neighborhood of 80μ, at four pressures in a cell of 77 cm. path, closed with quartz windows. Our vacuum spectrometer employed a plane echlette grating of 1.636 mm. spacing, consisting of a stack of glass plates of equal thickness. These were arranged in step fashion and the polished edges formed the reflected surface of the grating. The spectrometer had slits 1.25 mm. wide and a focussing collimating mirror of 50 cm. focal length.

Figure 1 indicates the galvanometer deflection plotted against the spectrometer setting when the absorption cell was evacuated, and when filled to 2.5, 5, 10 and 20 cm. pressure of HCl gas. Each set of observations was repeated at least once with three exceptions. A small figure adjacent to a point indicates that two observations chanced to coincide. Through each set of points is drawn the most reasonable curve. It will be noted that the origin of ordinates has been successively displaced for the series of curves, for the purposes of clarity. For the observations beyond about 91μ the sensitivity of the apparatus was considerably increased, but on the plot all the deflections are reduced to the same scale. One may obtain an idea as to the probable experimental error from the figure. In few cases was the spread of points much greater than the possible error of reading. An error may be present due to the presence of shorter wave-lengths in high orders. We believe that this must be small since the light path included 4 mm. of quartz which greatly diminished the intensity of waves shorter than 45μ, and the grating was adjusted to give a weak second order of wave-lengths about 45μ. Short infra-red radiation was almost perfectly eliminated.

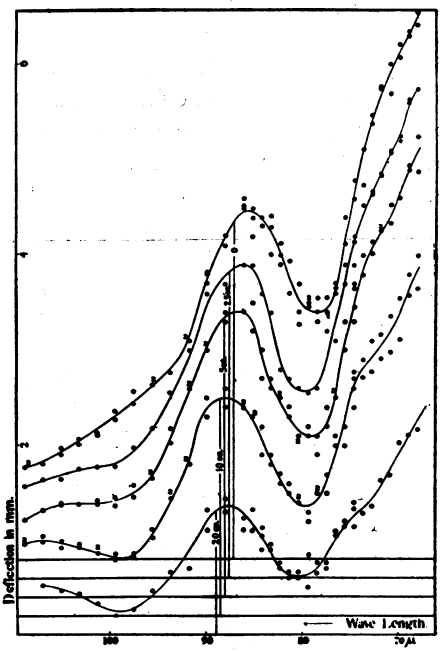

FIGURE 1
The intensity distribution in the background and absorption spectra.

In figure 2 the solid lines represent a plot of the differences in ordinate for the curve with evacuated cell and the other curves in succession of figure 1; in other words a plot of A, of the preceding discussion, against λ_s. Since, however, we have here three absorption lines which are incompletely resolved, it is necessary to divide the area under the solid curves into such parts as would be expected if it were possible to examine each line individually in the absence of others. The dotted lines indicate how this was done on the basis of assumptions which appear reasonable. In the upper corner of the figure are plotted the areas under the dotted curves for the line at 80.4μ as a function of pressure. This line is the one due to an increase in quantum number from 5 to 6. One may note several indications that the absorption lines broaden very appreciably with increase in pressure, among them being the shape of the last mentioned

curve which does not flatten out as rapidly at higher pressures as would be required for a constant width of line.

The tangent to this curve at the origin, which determines the value of β, is of course dependent on the division of the areas under the absorption curves. We believe, however, that the value which we have determined is not in error by more than ten per cent. We have found for n(76 cm. 22°)$\int\beta(\lambda,0)d\lambda$ the value 1.10×10^{-4} cm. Since the line is relatively narrow we may consider $d\lambda/d\nu$ constant across the line and obtain for $n\int\beta(\nu,0)d\nu$ the value 5.12×10^{10} sec.$^{-1}$.

The method for calculating from the integral absorption coefficient the value of B_{ij}, the average probability of transition from the initial to the final state with the absorption of radiation, has been indicated by Tolman and Badger.[2] Taking into account our present definition of β, and using the *a priori* probabilities for the respective quantum states given by the new theories, namely $2(i + {}^1/_2)$, where i is the quantum number of the state, we obtain for $B_{5,6}$ the value 4.7×10^{16}.

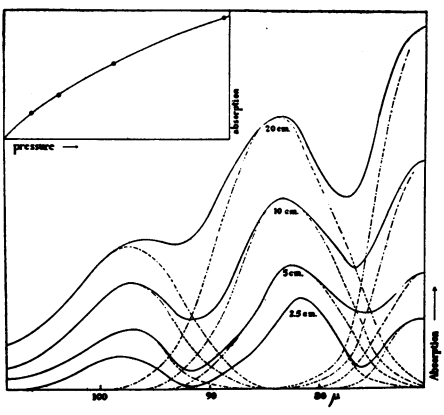

FIGURE 2
The absolute absorption curves.

In the new quantum theory developments the rotating molecule has received considerable attention and intensity relations have been derived in two different ways[3,4] involving the methods of Born, Heisenberg and Jordan; and of Schrödinger, respectively. The results are expressed in slightly different ways but when combined with the appropriate factors they seem both to lead to an expression for b_{ij}, the probability of absorption in unit density of radiation, of the following form

$$b_{ij} = \frac{8\pi^3\mu^2}{3h^2}\left(\frac{i+1}{2i+1}\right).$$

In this relation μ is an electric moment. If we may use the electric moment obtained from the dielectric constant by means of the Debye classical equation, b_{ij} may be evaluated. Substituting the value 1.034×10^{-18} c.g.s.u. which Zahn[5] obtained from his investigation on the dielectric constant of HCl, we obtain for $b_{5,6}$ the result, 1.12×10^{18}.

TABLE 1

LINE NO.	n(76 CM. 22°) $\int\beta(\nu,o)d\nu$	$B_{5,6}$ (EXPT.)	$b_{5,6}$ (THEORET.)
6	5.12×10^{10}	4.7×10^{16}	1.12×10^{18}

We have tabulated for comparison the probability of transition predicted by theory and that which is determined by experiment. Certainly the theoretical value fails to agree in magnitude with the experimental one by an amount much greater than the possible experimental error.

One may say, perhaps, that some factor must still be introduced in the theoretical expression to obtain the correct magnitude of b_{ij}; and the experimental observations offer a means of evaluating this. But, unfortunately, the theoretical probabilities do not have even the right relative values. They decrease with quantum number while for the experimental values Tolman and Badger found a decided increase. The absolute values which they calculated may be in error for the reasons given above, but more perfect resolution would be expected to increase the trend they observed rather than to eliminate it. It would seem, therefore, that the predictions of the new quantum theory, while they may apply to some ideal system, do not describe the conditions we have experimentally observed in the case of hydrogen chloride.

In conclusion we wish to express our indebtedness to the Carnegie Institution of Washington for funds which made this work possible.

[1] Czerny, *Zeits. f. Physik*, **34**, 227 (1925).
[2] Tolman and Badger, *Phys. Rev.*, **27**, 383 (1926).
[3] Dennison, *Phys. Rev.*, **28**, 318 (1926).
[4] Reiche, *Zeits. f. Physik*, **41**, 453 (1927).
[5] Zahn, *Phys. Rev.*, **24**, 400 (1924).

NOTE ON "PENDULUM" ORBITS IN ATOMIC MODELS

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On the simple Bohr theory the orbit of an electron moving in a central field of force about the nucleus is designated by two quantum numbers n and k, of which the first is called the principal quantum number and the second the azimuthal or auxiliary quantum number. These numbers are allowed to take all integral values (for a given orbit $k \leq n$) except zero. It will be seen that for $k = 0$ we get an orbit which is a straight line passing through the nucleus. This type of orbit is commonly known as a "pendulum" orbit and has been usually ruled out of the system of actual orbits because it involves collision of the electron with the nucleus. Nevertheless the fact that the *energy* of an electron orbit under the conditions specified above depends only on the principal quantum number and not on the azimuthal quantum number suggests the possibility of getting